

## PATENT ABSTRACTS OF JAPAN

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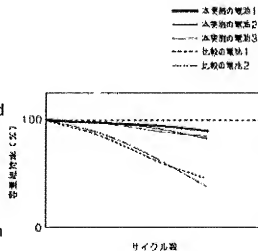
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FUJIWARA SHOZO(54) MANUFACTURING METHOD OF PASTE FOR POSITIVE ELECTRODE OF LITHIUM  
SECONDARY BATTERY

## (57)Abstract:

PROBLEM TO BE SOLVED: To improve dispersibility of a positive electrode active material, an electrical conductive agent, and a bonding agent by improving a manufacturing method of a paste for the positive electrode of a lithium secondary battery, and to provide a battery, which suppresses capacity variation in the battery manufacture and degradation in the charging/discharging capacity in repeated charging/discharging.

SOLUTION: In a paste for electrodes obtained by kneading and dispersion of a positive electrode active material having a lithium containing transition metal composite oxide as main substance, a conductive agent, and a binder into a solvent, a surfactant is added and dispersed into the solvent before adding and dispersing the binder.



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CLAIMS

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[Claim(s)]

[Claim 1]By a paste manufacturing process before being the method of manufacturing a paste for electrodes which consists of positive active material, a conducting agent, a binder, and a surface-active agent which made a subject a lithium containing transition metal multiple oxide and carrying out addition distribution of said binder. A manufacturing method of a paste for lithium secondary battery anodes carrying out addition distribution of the surface-active agent into a solvent beforehand.

[Claim 2]When setting to M2 (g) an addition of said surface-active agent which adds an addition of S (m2/g) and said conducting agent for specific surface area of said conducting agent to M1 (g) and said solvent and it is considered as  $R = S \times M1/M2$ , in  $10 < R < 10000$ , A manufacturing method of a paste for lithium secondary battery anodes of Claim 1 which carries out carrying out addition distribution of said surface-active agent to said solvent with the feature.

[Claim 3]A lithium secondary battery, wherein a paste for anodes obtained by Claim 1 or Claim 2 is used.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the manufacturing method of the paste for lithium secondary battery anodes.

[0002]

[Description of the Prior Art]By manufacture of the paste for anodes used for a lithium secondary battery, conventionally. When the dispersion of fluororesin was added and kneaded as a binder in positive active material, the conducting agent, and the kneading dispersion thing of a solvent, uneven-ization of the paste by fibrosis condensation of fluororesin arose, and the polar plate had in \*\*\*\*\* a problem which a pinhole generates. When a cell was produced using this paste, the paste coating to the charge collector became uneven, and capacity variation arose. There was a problem which reduces working efficiency by mixture peeling in order that an aggregate may weaken adhesion of a mixture and a charge collector, or causes the fall of charge-and-discharge capacity in order to worsen the current collection nature of a polar plate. Then, in order to control fibrosis condensation of fluororesin, to improve the dispersibility of positive electrode paste and to improve a battery characteristic, The dispersion which made the solvent carry out mixture dispersion of the binder to the kneading dispersion thing which carried out kneading dispersion of positive active material, a conducting agent, and the solvent is produced, respectively, The method of adding the kneading dispersion thing which carried out kneading dispersion of the former positive active material, a conducting agent, and the solvent in the dispersion of the latter binder, and manufacturing the paste for anodes was adopted.

[0003]

[Problem(s) to be Solved by the Invention]However, although the problem, as for, the binder under paste carries out fibrosis condensation improves with this paste manufacturing method for anodes, The pinhole produced in \*\*\*\*\* which distribution of the conducting agent to a solvent is difficult for harder [ with small compatibility with the solvent of a conducting agent ], and many aggregates of a conducting agent exist harder easily, and originates in it as a result in an electrode surface at this

aggregate. Therefore, after positive-electrode-paste spreading desiccation, since the binding property of active materials and the adhesion of an electrode compound and a charge collector were weak, exfoliation of the electrode compound from a charge collector and omission arose, and the problem of causing the fall of service capacity and aggravation of a load characteristic was also during repetition charge-and-discharge use.

[0004]This invention solves the above SUBJECT, and loses the electrode surface defect in the case of paste coating, and an object of this invention is to control the battery characteristic fall by condensation-izing of the paste produced from fibrosis of a binder.

[0005]

[Means for Solving the Problem]In order to attain the above purposes, this invention is a front paste manufacturing process rather than carrying out addition distribution of the binder into a solvent, Addition distribution of the surface-active agent is beforehand carried out into a solvent, and kneading dispersion of positive active material, a conducting agent, and a binder which made a subject a lithium containing transition metal multiple oxide is carried out into a solvent.

[0006]If a paste for anodes is manufactured using this invention, improvement in compatibility to a solvent of a conducting agent, High decentralization of a conducting agent in inside of a solvent is urged, it becomes possible to control generating of an aggregate of a conducting agent, and an electrode surface defect resulting from this aggregate, and uniformly coating of positive electrode paste and the adhesion of an electrode compound and a charge collector can be strengthened. As a result, there is an effect which makes it hard to peel in a mixture in positive electrode plate manufacture, and can control a problem and electrode cycle degradation of improvement in workability in a manufacturing process and capacity variation of a cell.

[0007]As a surface-active agent used at this time, a polyoxyethylene nonylphenyl ether system, They are mentioned by non-ion system surface-active agents, such as a polyoxyethylene octylphenyl ether system, and as a binder, Polytetrafluoroethylene resin (PTFE), fluoro AKOKISHI resin (PFA), ethylene propylene fluoridation resin (FEP), etc. are mentioned, and solution which dissolved water soluble polymers, such as carboxymethyl cellulose, as a thickener is mentioned to a solvent. Black lead system material, conductive carbon black, etc. are mentioned to a conducting agent.

[0008]On a process of producing positive electrode paste, addition, into a solvent of a surface-active agent and the kneading dispersion can obtain a paste for anodes equivalent to this invention in any order, if that is addition and before carrying out kneading dispersion, about a binder.

[0009]

[Embodiment of the Invention]Hereafter, one working example of this invention is described. Although used water as a solvent, acetylene black (AB) was used as a conducting agent and polyoxyethylene nonylphenyl ether was used as a surface-active agent, the same effect can be acquired if a suitable surface-active agent is applied to the combination of a solvent and a conducting agent.

[0010]

[Example](Working example 1) The manufacturing method of the anode board 5 is explained first.

First, carboxymethyl cellulose was used as a thickener, the solution which dissolved thickener 1 mass part in water 99 mass part was produced, and this solution was used as the solvent. Thus, the aqueous paste 1 produced by adding 50 mass parts and 1.5 mass parts of conducting agents to solvent 30 produced mass part, and carrying out kneading dispersion of the  $\text{LiCoO}_2$  powder to it as positive active material was produced. As a conducting agent, acetylene black (AB) which is one of the conductive carbon black was used. Next, when setting to M2 (g) the addition of the surface-active agent which adds the addition of S (m<sup>2</sup>/g) and a conducting agent for the specific surface area of a conducting agent to M1 (g) and a solvent, When [ of the surface area of the conducting agent to the amount of unit surface-active agents ] R was comparatively defined as  $R = S \times M1 / M2$ , it added and kneading dispersion of the polyoxyethylene nonylphenyl ether 0.37 mass part as a surface-active agent was carried out to the aqueous paste 1 so that it might be set to  $R = 1000$ . Then, as a binder, it 3-mass-parts-added, kneading dispersion of the polytetrafluoroethylene (PTFE) 50 mass-part solution was carried out, and positive electrode paste was obtained.

[0011]Next, the die coater was used for the 20-micrometer-thick aluminium foil using the paste for anodes of this this invention as a charge collector, the thickness of one side was 180 micrometers, double spread was carried out, it dried and the anode board was heated at 200 to 300 which is the melting temperature of PTFE \*\*. Then, it rolled and cut in thickness of 0.18 mm, and the anode board was produced. The surface state of the anode board obtained at this time was checked. The above-mentioned anode board was used as the polar plate 1 of this example.

[0012]The manufacturing method of the negative electrode plate 6 is explained. First, mixture dispersion of the solution 23 mass part which received styrene-butadiene-rubber 5 mass part as scaly graphite powder 50 mass part and a binder, received carboxyl methyl cellulose 1 mass part as a thickener, and was dissolved in water 99 mass part was carried out, and the paste for negative electrodes was obtained. Spreading desiccation of the obtained paste for negative electrodes was carried out to both sides of the negative pole collector which consists of 40-micrometer-thick copper foil using a die coater, it rolled and cut in thickness of 0.2 mm, and the sheet shaped negative electrode plate 6 was produced. The electrolysis solution used for the mixed liquor used as methyl propionate 20vol% what dissolved  $\text{LiPF}_6$  in the concentration of 1 mol/liter diethyl carbonate 50vol% ethylene carbonate 30vol% in 25 \*\*. This electrolysis solution is accommodated in a cell case, is impregnated in a positive active material layer and a negative electrode active material layer, and bears movement of the Li ion between the anode board 5 and the negative electrode plate 6 through the very small hole of a porosity separator in a cell reaction.

[0013]A cell case consists of the insulating gasket 2 which insulates between the case body 8 which obtained the stainless steel plate of organic electrolysis-proof acidity or alkalinity by carrying out deep-drawing shaping, the obturation board 1, and the obturation boards 1 and the case bodies 8.

[0014]One embodiment of the lithium secondary battery of this invention is a cylindrical lithium secondary battery as shown in drawing 1, and consists of a group of electrode, an electrolysis solution, and a cell case that accommodates these. A group of electrode consists of the separator

7, the positive electrode lead 3, the negative electrode lead 9, the top electric insulating plate 4, and the lower electric insulating plate 10 of the sheet shaped which insulates between the sheet shaped anode board 5, the sheet shaped negative electrode plate 6, and the anode board 5 and the negative electrode plate 6. The anode board 5 carries out application formation to both sides of aluminium foil. The separator 7 is a porous polypropylene film, these pile it up, is wound spirally and is just accommodated in the cylindrical case body 8. The cell produced the thing of 17 mm in diameter, and height 50mm size.

[0015]Thus, the cell was produced and the initial service capacity and cycle characteristic were checked. Before producing a cell, the mass of the positive electrode plate used for the cell was measured, and it compared with initial service capacity.

[0016]The above-mentioned cell was used as the cell 1 of this example.

[0017](Working example 2) the surface area of the conducting agent to the amount of unit surface-active agents -- so that  $R(= SxM1/M2) = 15000$  may be held comparatively, Except having blended the conducting agent and the surface-active agent into the solvent, the anode board produced on the same conditions as working example 1 of this invention was used as the polar plate 2 of this example, and the cell using this was used as the cell 2 of this example.

[0018](Working example 3) the surface area of the conducting agent to the amount of unit surface-active agents -- so that  $R(= SxM1/M2) = 3$  may be held comparatively, Except having blended the conducting agent and the surface-active agent into the solvent, the anode board produced on the same conditions as working example 1 of this invention was used as the polar plate 3 of this example, and the cell using this was used as the cell 3 of this example.

[0019](Comparative example 1) In the carboxymethyl cellulose solution used as the solvent, positive active material, The conducting agent and the binder were added, the paste for anodes was produced, and it was considered as working example 1 of this invention, and the polar plate 1 of comparison of the anode board produced on the same conditions also as the procedure after spreading to the charge collector of a paste, and the loadings of each structure material, and was considered as the cell 1 of comparison of the cell using this.

[0020](Comparative example 2) In the carboxymethyl cellulose solution used as the solvent, positive active material, For a conducting agent and a binder, addition and after carrying out kneading dispersion, a surface-active agent Addition, after carrying out kneading dispersion and producing the paste for anodes, It was considered as working example 1 of this invention, and the polar plate 2 of comparison of the anode board produced on the same conditions also as the procedure after spreading to the charge collector of a paste, and the loadings of each structure material, and was considered as the cell 2 of comparison of the cell using this.

[0021]The anode board obtained by above-mentioned this examples 1, 2, and 3 and the comparative examples 1 and 2 was evaluated as shown below. The number of the aggregate which exists in 1000 cm of anode board [ two ] surface, and pinholes was calculated by viewing, and it was shown in Table 1.

[0022]

[Table 1]

	凝集塊数	ピンホール数
本実施の極板1	2	0
本実施の極板2	8	1
本実施の極板3	5	2
比較の極板1	53	12
比較の極板2	43	10

[0023]From the result of (Table 1), with the polar plate 1 of this example, there is almost no aggregate which the aggregate of AB and PTFE fibrose and produce, and it is surmised that this is because the surface-active agent existed in proper quantity to the amount of conducting agents in the field of  $10 < R < 10000$  and sufficient distribution of the conducting agent in the inside of a solvent was performed.

[0024]Although the aggregate of AB and the pinhole were slightly observed in the polar plate 2 of this example, Since the amount of surface-active agents added to a solvent in the field of  $10000 < R$  was slightly insufficient for this to the amount of conducting agents to add, it is surmised that it is because distribution of the conducting agent in the inside of a solvent became uneven locally, but. When the number of an aggregate and electrode surface defects is compared with the comparative examples 1 and 2, it is thought that there was little the quantity and there was an effect of the generation control of an aggregate and an electrode surface defect.

[0025]In the polar plate 3 of this example, excessive surface-active agents became an aggregate, and since distribution of AB or a binder was checked or re-condensation of AB was urged, the aggregate of AB was observed slightly. However, when the quantity of an aggregate and an electrode surface defect is measured with other working example and a comparative example, it is less than the effect in working example 1, but it is thought on a par with working example 2 that there was little generating of an aggregate and an electrode surface defect, and there was an effect of control of those defective generating.

[0026]On the other hand, in the polar plate 1 of comparison which has not added the surface-active agent at all to a solvent, many aggregates with insufficient distribution of AB and AB from which the compatibility of a solvent happens harder [ small ], and aggregates from which binder PTFE moreover added started fibrosis arose.

[0027]In the comparative polar plate 2, the aggregate of PTFE which fibrosed, and the aggregate by which AB was confined in PTFE which fibrosed further were observed, and, for this reason, many pinholes produced in \*\*\*\*\*. Before adding a surface-active agent, this has insufficient distribution of a conducting agent in a solvent, and causes fibrosis condensation, and PTFE A sake, Even if AB is confined in PTFE which caused this fibrosis, an aggregate is produced and it adds a proper quantity of surface-active agents behind, it is guessed since it was impossible to have re-dispersion-ized AB inside the aggregate which consists of this AB and PTFE.

[0028]The cycle life property of the cell using these anode boards and this invention article is shown in drawing 2.

[0029] Charge was performed by 500-mA constant current, when set to 4.1V, it changed with the constant potential charge of 4.1V, and charge was performed for a total of 2 hours. When discharge was performed by 20 \*\*720 mA and discharge potential was set to 3.0V, discharge was ended and the next charge was started. Even if the cells 1, 2, and 3 of this example repeated charge and discharge from this drawing 2 to the comparative examples 1 and 2, there was little degradation of capacity, and it turned out that it excels in the cycle characteristic. The dispersibility of the cell of this example in the inside of the solvent of positive active material, a conducting agent, and each binder improves, since adhesion with the charge collector of positive electrode mixture was improved, also expansion contraction of the mixture in charge and discharge, a mixture does not peel easily from a charge collector, the current collection nature of an active material is held, and this is considered that the battery characteristic has been improved.

[0030] The amount of mean pole plate qualities and the initial service capacity of the cycle were measured by the cell of working example and the comparative example which were shown above, the amount variation of plate qualities and the variation of the initial capacity of a cycle test were calculated very much from the following formula, and the maximum of the variation acquired from those calculation results was shown in Table 2. Initial service capacity used the service capacity in the early stages of a cycle test.

[0031] It was defined as  $\text{difference} \div \text{average value} \times 100$  with variation (%) =  $\text{average value}$ .

[0032]

[Table 2]

	極板質量平均値からの バラツキ最大値	初期放電容量平均値からの バラツキ最大値
本実施の極板1	0.10%	0.15%
本実施の極板2	0.15%	0.27%
本実施の極板3	0.13%	0.24%
比較の極板1	0.62%	1.49%
比較の極板2	0.64%	1.54%

[0033] As shown in (Table 2), the paste for anodes produced by this invention could perform uniform spreading of the mass stable as compared with the comparative examples 1 and 2, and the variation in the produced positive electrode mass and the initial capacity of the cell using this electrode became small. Since this could lose the electrode surface defect, such as coating \*\*\*\* by the aggregate of a conducting agent and a binder, and a pinhole, and applied the paste for anodes of this invention to the charge collector uniformly, it can suppress small positive electrode plate mass and the initial capacity variation of a cell, and is considered that the effect showed up.

[0034] After saving these cells 60 \*\* for 20 days by the charging state and performing charge and discharge several times at ordinary temperature after that, capacity until it discharges at 720 mA and voltage amounts to 3.0V was calculated, and the rate over the capacity before the preservation was shown in Table 3.

[0035]



[Table 3]

充電サイクル特性	(保存後の容量／保存前の容量) × 100
本実施の電池1	99
本実施の電池2	97
本実施の電池3	97
比較の電池1	85
比較の電池2	86

[0036]Also in high temperature preservation, this invention article became clear [ that capacity deterioration decreases ] as shown in Table 3.

[0037]

[Effect of the Invention]As explained above, according to this invention, in use of repetition charge and discharge, degradation of charge-and-discharge capacity and degradation of a load characteristic can be suppressed very small. Since the paste for anodes of this invention can be uniformly applied to a charge collector, it can suppress the capacity variation of a cell small in the case of battery manufacturing. Degradation of charge-and-discharge capacity and degradation of a load characteristic can be small suppressed under a severe condition which is neglected under an elevated temperature over a long period of time. Since the electrode surface defect in the case of the paste coating by the aggregate of a binder is furthermore lost and the adhesion of positive electrode mixture and a charge collector can be improved, fall of the mixture in a battery assembly process is lost, and workability can be improved.

[Translation done.]